Change in cation nonstoichiometry at interfaces during crystal growth in polycrystalline BaTiO$_3$

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Using an embedded single crystal in a polycrystalline matrix and quantitative electron energy loss spectroscopy, we have demonstrated that Ti-excess grain boundary nonstoichiometry can vary with the extent of boundary migration. While a slight excess in Ti was detected at the boundaries between small matrix grains, a large increase in Ti/Ba ratio, to as much as $\sim$1.50 compared to the stoichiometric value, was present at the interface between a growing single crystal and the matrix grains when the embedded crystal grew up to a few hundred micrometers. This change in nonstoichiometry was attributed to a continuous accumulation of excessive Ti at the moving boundary during crystal growth. The present result indicates that growth kinetics can critically affect the interface chemistry in polycrystals. © 2006 American Institute of Physics.

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For over several decades, interfacial segregation has been intensively studied in both metallic and ceramic systems$^{1-5}$ under the understanding that the physical properties of materials are governed largely by the characteristics at interfaces, including surfaces and grain boundaries. Even since the well-known simple model proposed by Langmuir for gas adsorption on a solid surface,$^6$ a number of studies on the equilibrium segregation at interfaces have been well documented.$^{1-3}$ Recent experimental observations and nanometer-scale analysis using transmission electron microscopy$^{7-12}$ (TEM) have also directly demonstrated that variations in structure and composition at interfaces play a key role in materials performance. Most of the previous investigations, however, have been focused on the equilibrium segregation for given thermodynamic conditions.

When a crystal grows quickly, the interfaces may not be under thermodynamic equilibrium. In particular, some of the ABO$_3$-type perovskite titanates, such as BaTiO$_3$ and SrTiO$_3$, have peculiar grain growth behavior, showing abnormally fast growth of some selective grains with strongly suppressed growth of other grains in polycrystalline samples, so-called abnormal grain growth.$^{13-15}$ In such a case, kinetic factors should then affect the chemical composition. By using electron energy loss spectroscopy (EELS) in TEM, the present investigation demonstrates systematically that the growth kinetics of grains strongly affects the Ti segregation and resultant cation nonstoichiometry at grain boundaries in a model system BaTiO$_3$.

To prepare 0.4 mol% TiO$_2$-excess BaTiO$_3$ powder a mixture of BaTiO$_3$ (99.8%, Fuji Titanium, Japan) and TiO$_2$ (99.9%, Aldrich, USA) was ball-milled in ethyl alcohol for 24 h using a polyethylene bottle and zirconia balls. The dried slurry was crushed and sieved to 125 μm. A BaTiO$_3$ single crystal (Ceracom Ltd., Asan, Korea) having {111} and {110} planes was cut into small pieces of $1 \times 1 \times 5$ mm in size. A single crystal piece was embedded within the Ti-excess BaTiO$_3$ powder compact, and isostatically pressed under 200 MPa. The pressed pellet containing the single crystal was annealed at 1350 °C for 5 h in air.

The microstructure of the samples was observed under an optical microscope and the grain boundary structure was examined using high-resolution electron microscopy (HREM, JEM-4010, operated at 400 kV, JEOL, Tokyo, Japan). A transmission electron microscope equipped with a field-emission gun (EM-002BF, operated at 200 kV, Topcon, Tokyo, Japan) was also utilized to analyze the chemical composition variation across the grain boundaries and the interfaces between the growing single crystal and the polycrystalline matrix grains. Since the peaks of the Ba L$_\alpha$ line and the Ti K$_\alpha$ line in energy dispersive spectroscopy (EDS) spectra overlap each other, the EDS-based composition measurement is not possible for quantitative chemical analysis in BaTiO$_3$. Composition change in Ba and Ti across the boundaries was quantitively measured by EELS (Gatan Enfina) using an electron probe size of 0.5 nm.

Figure 1(a) is a schematic showing the growth of the single crystal embedded in the polycrystalline matrix and Fig. 1(b) shows an optical micrograph of the region marked by a rectangle in Fig. 1(a). As shown in this figure, the growth shape is anisotropic, indicating that the growth rate of BaTiO$_3$ varies with crystallographic orientation, consistent with a previous report on BaTiO$_3$ crystal shape.$^{16}$ As a result, the development of facet planes during crystal growth is easily observed. While the (110) interface plane remains
parallel to the initial surface of the single crystal, the (02\bar{1}) and (201) planes are shown to be developed during growth. This growth shape clearly shows that the crystal has grown much faster along the [11\bar{1}] direction than along the [110] direction. On the other hand, the matrix grains have hardly grown, as shown in the inset of Fig. 1(b). Since the fast growth of some selective grains in a fine matrix is common in polycrystalline BaTiO₃, our model experiment of single-crystal growth allows us to systematically study the kinetic segregation during fast grain growth in real samples.

Figure 2(a) is a typical HREM image of a grain boundary in the fine matrix region indicated by A in Fig. 1(b). As shown in the figure, no intergranular phase is present at the boundary, showing a direct crystal-crystal interface. However, EELS analysis across the boundary within an interval of ~1.5 nm from the boundary core [Fig. 2(b)] reveals that excess Ti (Ti/Ba of ~1.10) is segregated at the boundary, compared with the stoichiometry (Ti/Ba=1) inside the bulk grain. The value of Ti/Ba of ~1.10 was almost the same (within 0.02) for five different grain boundaries, indicating that the segregation difference between boundaries was inconsiderable.

The chemical composition across the boundary between the growing single crystal and the matrix grains has also been measured. Compared with a constant Ti segregation of excess Ti (Ti/Ba of ~1.10) at the boundaries between fine matrix grains, the Ti segregation between the growing crystal and the matrix grains increased with growth of the crystal, as shown in Figs. 2(d) and 2(f). Figure 2(c) shows the HREM image of the interface parallel to the initial (110) plane, denoted by B in Fig. 1(b), with crystal growth of less than 100 \mu m and Fig. 2(d) shows the EELS result across its interface. As in the case of the boundaries between fine matrix grains (region A), no intergranular phase is observed. However, the Ti-excess nonstoichiometry is ~1.17 in Ti/Ba, more pronounced than that in region A with no grain growth. Since the quantitative analysis in EELS can be affected by the crystallographic orientation of the crystal surface, the

FIG. 1. (Color online) (a) A schematic of the growth of the single crystal embedded in the polycrystalline matrix. (b) An optical micrograph of the region marked by a rectangle in (a).

FIG. 2. (Color online) HREM images of the boundary (a) in the fine matrix region indicated by A in Fig. 1(b) and the boundaries between the crystal and the fine matrix indicated by (b) B and (c) C in Fig. 1(b). (b), (c), and (d) EELS analyses across the boundaries within an interval of ~1.5 nm from the boundary core at the interfaces in (a), (c), and (e), respectively.
composition of the embedded single crystal far from the interface was taken as the reference. This result suggests that more adsorption of Ti ions at grain boundaries occurred with the crystal growth.

Compelling evidence of kinetic segregation of Ti ions with crystal growth is shown in Fig. 2(f), which is the EELS profile across the boundary between the developed [210] plane of the growing crystal and a matrix grain, interface C in Fig. 1(b). In this case, with crystal growth of a few hundred microns, the Ti segregation is more than 1.50 in Ti/Ba. The present series of quantitative EELS analyses thus demonstrates that the segregation of Ti ion of the interface between the single crystal and the matrix grains is enhanced as the crystal grows. Since grain growth, which is induced by the size difference between grains, is impeded by solute segregation, the present result also shows that Ti ion segregation at grain boundaries in polycrystalline BaTiO$_3$ can be promoted by grain growth.

Titanium excess at grain boundaries in TiO$_2$-excess BaTiO$_3$ has also been observed and measured in previous investigations. The measured Ti segregation at grain boundaries between fine matrix grains [Fig. 2(b)] is in accord with a previous result. Since the size of the fine grains in the matrix region was practically invariable at $\sim$3 $\mu$m in size during annealing for 5 h in air, it is thought that a Ti/Ba ratio of $\sim$1.10 was the equilibrium nonstoichiometric value at the grain boundary at 1350 °C in air. In contrast, the embedded single crystal has grown rapidly, consuming the fine matrix grains, during the air annealing. Therefore, the Ti segregated at the boundaries between the fine matrix grains must be continuously accumulated at the moving interface of the single crystal, resulting in an increased Ti-excess cation nonstoichiometry with crystal growth. Such kinetic Ti accumulation at grain boundaries can be understood as the adsorption of solutes, which is similar to the model of monolayer gas adsorption proposed by Langmuir. However, it must be impossible for the crystal boundaries to accommodate the excessive Ti without limit. Multiple adsorbed layers are expected to form at grain boundaries with further crystal growth. Figure 3 shows a nanometer-thick intergranular amorphous film formed at interface C after additional annealing at 1350 °C for 20 h, as in a previous investigation. This HREM result confirms the formation of multiple Ti adsorption layers at grain boundaries and further the formation of a Ti-excess amorphous phase. Strong Ti segregation at grain boundaries in BaTiO$_3$ can therefore be induced kinetically.

Most of the previous investigations on interfacial segregation have concerned the segregation at thermodynamical equilibrium. The present study shows that grain boundary segregation in polycrystalline materials can be critically affected by kinetic processes, such as crystal growth, in addition to thermodynamic factors. Therefore, processing conditions need to be carefully determined to control the composition at grain boundaries in multicomponent systems. In summary, we have investigated the kinetic change in cation nonstoichiometry at grain boundaries in a BaTiO$_3$ model system with a single crystal embedded in a polycrystalline matrix. Quantitative EELS analysis showed that the segregation of Ti ions at the boundaries between the growing single crystal and the fine matrix grains was intensified with crystal growth. The increased segregation has been attributed to the continuous accumulation of the excess Ti present at grain boundaries between fine matrix grains during crystal growth. When the crystal grew further and hence the accumulation became excessive, an intergranular amorphous film formed at the interface of the single crystal. The present observation thus demonstrates that the boundary segregation can kinetically be intensified, in other words, the adsorption layer can thicken with grain growth.

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